

# The seasonal cycle of N<sub>2</sub>O

Ting Liao,<sup>1</sup> Charles D. Camp,<sup>2</sup> and Yuk L. Yung<sup>3</sup>

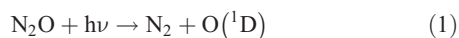
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[1] We have carried out an empirical study of the seasonal cycle of nitrous oxide (N<sub>2</sub>O) using the data archived by the National Oceanic and Atmospheric Administration – Climate Monitoring and Diagnostics Laboratory (NOAA-CMDL) Global Cooperative Air Sampling Network from 1977 to 2000. In order to isolate the seasonal cycle, we first detrended the data using least square polynomial fits. The remaining variability was averaged to extract the seasonal cycle, which has an amplitude of about 0.8 ppbv. The statistical significance of the seasonal signal was established using the multitaper method and Welch's method for power spectrum analysis. **INDEX TERMS:** 0341 Atmospheric Composition and Structure: Middle atmosphere—constituent transport and chemistry (3334); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 1610 Global Change: Atmosphere (0315, 0325). **Citation:** Liao, T., C. D. Camp, and Y. L. Yung (2004), The seasonal cycle of N<sub>2</sub>O, *Geophys. Res. Lett.*, 31, L17108, doi:10.1029/2004GL020345.

## 1. Introduction

[2] The present terrestrial atmosphere contains about 320 ppbv (nmol/mol) of nitrous oxide (N<sub>2</sub>O). N<sub>2</sub>O is produced mainly by microbes in nitrification and denitrification processes. On a per molecule basis it is 200 times as effective as CO<sub>2</sub> in causing global warming in the atmosphere. A doubling of atmospheric N<sub>2</sub>O, for example, would cause the mean global surface temperature to increase by 0.7°C [Wang *et al.*, 1976; Houghton *et al.*, 1990], which is approximately the total observed mean global warming in the last hundred years. As a consequence, N<sub>2</sub>O is one of the gases targeted for regulation by the Kyoto Protocol (1997).

[3] N<sub>2</sub>O is removed from the atmosphere primarily by UV photolysis



A smaller loss occurs from the (photo-oxidation) reaction with O(<sup>1</sup>D)



[4] Both reactions (1) and (2) take place primarily in the stratosphere, resulting in a mean lifetime of 120–150 years

for N<sub>2</sub>O [Minschwaner *et al.*, 1993; Olsen *et al.*, 2001]. Reaction (2a) is the major source of odd nitrogen (NO<sub>x</sub>) in the stratosphere and plays a fundamental role in regulating the ozone layer [McElroy and McConnell, 1971; Crutzen, 1971; Nicolet and Vergison, 1971; Logan *et al.*, 1978; Wennberg *et al.*, 1994]. Note that a consequence of the above reactions is that the mixing ratio of N<sub>2</sub>O in the stratosphere is depleted relative to that in the troposphere.

[5] The seasonal cycle of a trace molecule in the atmosphere provides valuable information of its sources, sinks and transport processes in the atmosphere. It is therefore surprising that we have no information on the seasonal variability of N<sub>2</sub>O. The main reason is that the lifetime of N<sub>2</sub>O is much longer than a year, and the expected change in the concentration over a season is very small. In this paper we show that the current data can be analyzed to reveal the seasonal cycle of N<sub>2</sub>O. A potential explanation is the mixing in the spring of N<sub>2</sub>O-poor stratospheric air with N<sub>2</sub>O-rich tropospheric air.

## 2. Data and Analysis

[6] N<sub>2</sub>O data is archived by the National Oceanic and Atmospheric Administration – Climate Monitoring and Diagnostics Laboratory (NOAA-CMDL) Global Cooperative Air Sampling Network from 1977 to 2000 and is divided into two separate data sets [Hall *et al.*, 2002] (data available at ftp://ftp.cmdl.noaa.gov/hats/n2o/flasks/). The first set contains the concentrations of N<sub>2</sub>O measured before 1996, while the other contains those measured after 1996. Although it seemed reasonable to use both sets of data to calculate the seasonal cycle, we found that the fluctuations of the concentrations in the two data sets were obviously different (data not shown). Due to the limited amount of post-1996 data, we were not able to tell whether the difference was caused by systematic error. Therefore, for this study, we restricted our analysis to the data obtained before 1996.

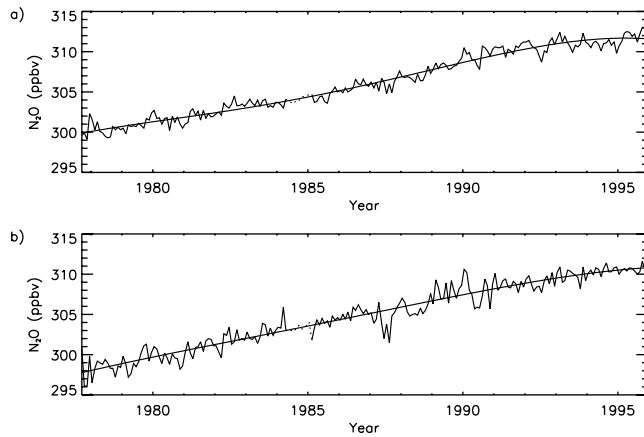
[7] The global data in each set are divided into Northern Hemisphere (NH) and Southern Hemisphere (SH) averages. The NH data were taken at Alert (Northwest Territories, Canada), Barrow (Alaska), Mauna Loa (Hawaii) and Niwot Ridge (Colorado). The SH data were taken at South Pole, Cape Grim (Tasmania, Australia) and Cape Matatula (American Samoa). There are more missing data in the SH than in the NH.

[8] The data between May, 1984 and January, 1985 are missing for all seven stations. In order to estimate the missing data points, we first used a least square polynomial fit to find the trend of the averaged data. We then removed the trend and calculated the mean concentration in each month to obtain the seasonal cycle. Finally, we inserted the seasonal cycle on top of the polynomial trend to estimate the

<sup>1</sup>Department of Physics, California Institute of Technology, Pasadena, California, USA.

<sup>2</sup>Department of Applied and Computational Mathematics, California Institute of Technology, Pasadena, California, USA.

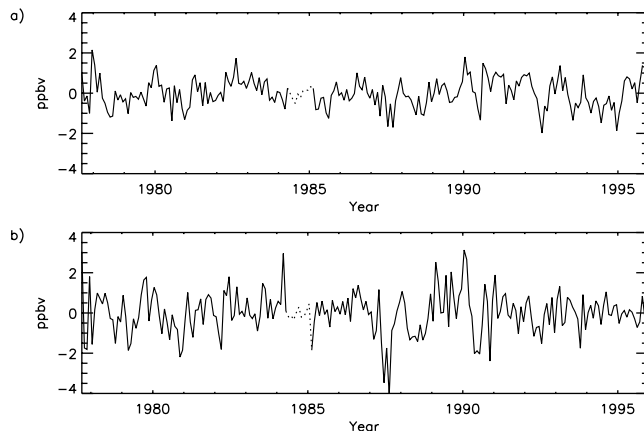
<sup>3</sup>Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, USA.



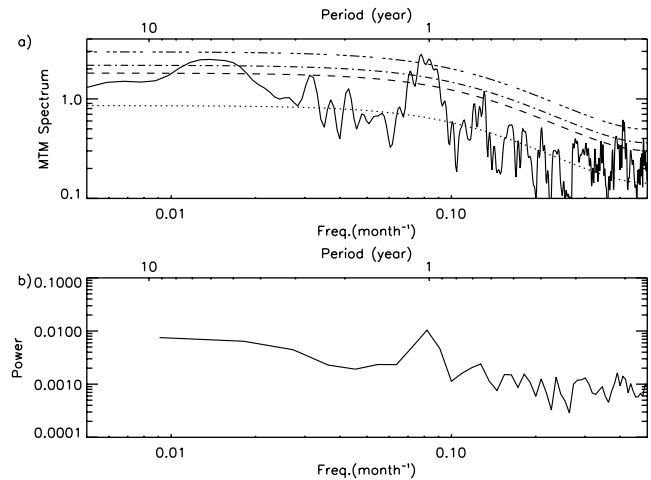
**Figure 1.** Measured concentration of N<sub>2</sub>O in a) northern hemisphere, and b) southern hemisphere, with 4th order polynomial fit (smooth solid line). Dotted points represent the interpolated data.

missing data. We then used this interpolated data to perform another polynomial fit. We compared a 4th order polynomial fit and a 5th order one (not shown) and found that they were very similar to each other, and we thus used the 4th order polynomial interpolation in all subsequent work. Figure 1 shows the polynomial fit for the interpolated data, where the dotted lines denote the estimates for the missing data. Figure 2 shows the detrended data for both hemispheres.

[9] To investigate the existence of a seasonal cycle, we analyzed the significance of the signal applying the multitaper method (MTM) [Ghil *et al.*, 2002]. MTM reduces the variance of spectral estimates by using a small set of tapers, thereby yielding a better and more stable estimate than do single-taper methods. The parameters of the MTM analysis must be chosen to give a good compromise between the required frequency resolution for resolving distinct signals and the benefit of reduced variance; following Ghil *et al.* [2002], we chose the resolution to be 2 and the number of tapers to be 3. The result for the NH data is shown in Figure 3a. From the figure we can see that there is a strong signal, i.e., at the 99% confidence level, with a period of about 1 year, which is the seasonal cycle. Since the way we interpolated the data could increase the significance of the



**Figure 2.** The detrended N<sub>2</sub>O concentration anomaly for a) northern hemisphere, standard deviation = 0.7125, and b) southern hemisphere, standard deviation = 1.0413.



**Figure 3.** Estimate of the power spectrum of the northern hemisphere data using a) Multitaper method. Dotted line represents the median. The dashed lines represent respectively 90%, 95% and 99% confidence of significant deviation above the mean. Also estimated using b) Welch power spectrum with a Hamming window.  $M = 110$  points,  $K = 3$  segments.

seasonal cycle, we performed the same analysis on the data with only a polynomial trend for the missing data (data not shown), and the result is hardly distinguishable. This was expected, since the length of the missing data is less a year, while our data set is more 20 years long. Several other significant peaks are found in the analysis, but in the present work we choose to focus on the one at 1 year, which represents the seasonal cycle.

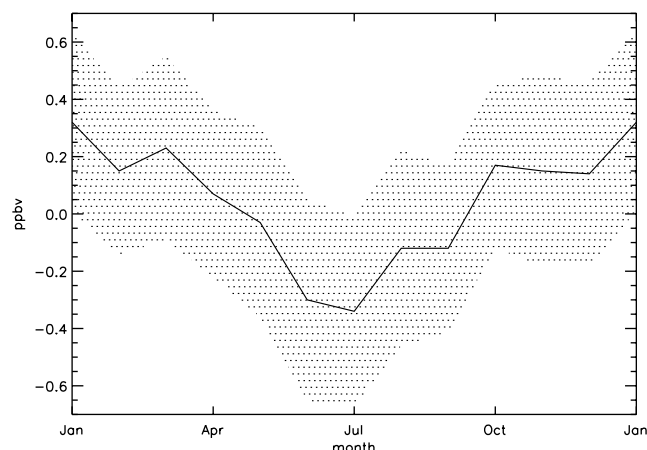
[10] For comparison, all spectra are also estimated by Welch's method [Press *et al.*, 1992] averaging the spectra of three half-length segments with 50% overlap, with a Hamming window applied to each segment prior to calculating its spectrum. Figure 3b shows the results of this analysis. It is again very clear that there is a strong signal with a period of 1 year. Therefore, there in fact exists a seasonal cycle in the concentration of N<sub>2</sub>O in the northern hemisphere.

[11] We used the same approach seeking a seasonal cycle in the SH data, but did not see a significant signal. As can be seen in Figure 2b, the SH data have much greater variability. The standard deviation of the detrended N<sub>2</sub>O data in this figure is 1.04 ppbv, or 46% larger than that for the NH data. In what follows, we shall be looking at only the NH data.

[12] We obtained the seasonal cycle by averaging the concentration of the detrended data for each month; the result is shown in Figure 4 (solid line). An estimated error for the seasonal cycle, Figure 4 (shaded region), was calculated in the following manner. The monthly concentrations,  $x_i$ , were measured with varying precision; let  $\sigma_i$  denote the standard error for each measurement. Weighted means,  $\mu$ , and standard errors of the means,  $\sigma$ , for each of the 12 months were then determined by

$$\mu = \frac{\sum_i \omega_i x_i}{\sum_i \omega_i} \quad \sigma^2 = \frac{1}{\sum_i \omega_i}, \quad (3)$$

where the weights are defined by  $\omega_i = 1/\sigma_i^2$ .



**Figure 4.** Seasonal cycle of N<sub>2</sub>O derived from monthly weighted means (solid line). Shaded area represents the estimated error for the seasonal cycle.

[13] We have also examined other N<sub>2</sub>O datasets. The Atmospheric Lifetime Experiment (ALE), the Global Atmospheric Gases Experiment (GAGE), and the Advanced Global Atmospheric Gases Experiment (AGAGE) have records for seven stations, three of which — Cape Matatula (14°S, 171°E), Cape Grim (41°S, 145°E) and Ragged Point (13°N, 59°W) — have ~25 years of data [Prinn *et al.*, 2000] (see also <http://cdiac.esd.ornl.gov/ndps/alegag.html>). Applying the same analysis technique (data not shown), we concluded that the seasonal cycles of N<sub>2</sub>O at Cape Matatula and Ragged Point were not significant at the 99% confidence level. Only the Cape Grim data (without including the years 1978–1986) showed a significant seasonal cycle at the 99% confidence level. The amplitude was 0.3 ppbv, or about half that of the NH signal. We also examined more recent data from the NOAA in situ network, Chromatograph for Atmospheric Trace Species (CATS) (J. E. Elkins, personal communication, 2004; [ftp://ftp.cmdl.noaa.gov/hats/n2o/insituGCS/CATS/global/insitu\\_global\\_N2O](ftp://ftp.cmdl.noaa.gov/hats/n2o/insituGCS/CATS/global/insitu_global_N2O)). However, this record (2000–2004) was too short to yield a robust seasonal cycle.

### 3. Discussion and Conclusions

[14] In the twenty years of N<sub>2</sub>O data from 1977 to 1996 in the northern hemisphere (NH), we sought a seasonal cycle for nitrous oxide. By applying both the multitaper method and Welch's method for spectrum analysis on the detrended N<sub>2</sub>O data, we found that there was a convincing seasonal cycle in the northern hemisphere, despite the fact that the lifetime of N<sub>2</sub>O is much longer than a year. The variability of the detrended data has a magnitude of about 3 ppbv, while the present terrestrial atmosphere contains about 320 ppbv of N<sub>2</sub>O. Since the magnitude of the seasonal cycle is less than 1 percent of the concentration, there were concerns about noise masking the seasonal cycle. The signal for the seasonal cycle of N<sub>2</sub>O is ±0.4 ppbv, a value that is indeed smaller than the total standard

deviation of 0.71 ppbv for the detrended N<sub>2</sub>O time series. Nevertheless, the seasonal cycle is significant at the 99% confidence level. We tried to do the same analysis on the southern hemisphere (SH) data but failed to extract a seasonal cycle signal due to the greater noise and the small expected seasonal signal.

[15] The seasonal cycle in the northern hemisphere shows an obvious decline around late spring to early summer. Preliminary modeling work based on Morgan *et al.* [2004] suggests that the minimum is strongly influenced by the seasonal influx of N<sub>2</sub>O-poor air from the stratosphere. This will be investigated in a follow-up paper.

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C. D. Camp, Department of Applied and Computational Mathematics, California Institute of Technology, Pasadena, CA 91125, USA.

T. Liao, Department of Physics, California Institute of Technology, Pasadena, CA 91125, USA.

Y. L. Yung, Division of Geological and Planetary Sciences, California Institute of Technology, Mail Stop 150-21, Pasadena, CA 91125, USA. (yly@gps.caltech.edu)